

(21) Application No. 36813/75 (22) Filed 8 Sept. 1975

(31) Convention Application No. 2 443 164

(32) Filed 10 Sept. 1974 in

(33) Federal Republic of Germany (DE)

(44) Complete Specification published 11 Oct. 1978

(51) INT CL² C09K 11/00

(52) Index at acceptance

C4S 33Y 650 70Y 714 715 716 71Y 720 722 725 729 72Y 730 734
738 73Y 747 748 74Y 750 751 756 76Y 774 782 783

B6A 42A 42D

C3K 127 400 DA

(54) THERMOPLASTIC SHEET CONTAINING
IRRADIATION-CONVERTING
PARTICLES

(71) We, HOECHST AKTIEN-GESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt (Main) 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to thermoplastic sheets containing irradiation-converting particles.

Sheet-like articles representing a certain value, for example documents or currency notes should have properties which, on the one hand, make falsification or forgery as difficult as possible, and, on the other hand, ensure an easy and rapid detection of such counterfeits.

Recently, thermoplastics have been used to an increasing extent for the manufacture of such articles, for example identity cards, cheque cards and credit cards. Composite materials, made of several of such sheets, are common. The composites may include other carriers, mostly printed, written or coated carriers, for example paper, photographs and magnetic layer carriers, and may also contain metals either as strips or complete layers.

In order to reduce risk of forgery, special printing inks as well as printing patterns, which can be copied only with great difficulty, are used. Furthermore, it is known to watermark the printing carrier or to mark it by means of dyed fibres. These methods, however, cannot be applied to plastics sheets, since, for example, an incorporation of fibres by the method used for paper causes processing troubles due to poor flow. Moreover, a substrate dyed in

different shades is, in many cases, undesirable: printing becomes more difficult to discern, especially under poor lighting conditions, and the substrate may be aesthetically displeasing. Furthermore, a mark visible without any auxiliary device is easily recognised by a potential forger, so that its protective value is diminished and the possibility of catching the user of a forged document or note in the act is reduced.

The present invention provides a thermoplastic sheet containing undissolved particles which convert invisible electromagnetic irradiation to visible light, in which sheet these particles, optionally in the presence of soluble or insoluble, finely distributed fluorescing substances imperceptible *per se*, are present in such a small amount that on irradiation the luminous effect produced by an individual particle, separately from the luminous effect of other particles of the same kind, may be perceived with the naked eye on a substrate which is either non-luminous or of a different luminosity, said particles having the forms of grains, small rods, filaments, or fibres, the grain size or thickness of the rods, filaments, or fibres being in the range of from 0.3 to 600 microns, preferably from 0.5 to 100, especially 1—30 microns and the length of the rods, filaments, or fibres in a range of 0.03 to 20 mm, preferably from 0.5 to 5 mm.

The particles are generally added to the sheet in amounts of from 0.3 to 10 weight %, preferably from 0.3 to 2 weight %, relative to the total weight of the sheet. In principle, amounts of less than 0.03 weight % and more than 10 weight % may also be used; however, amounts less than 0.03 weight % may result in a displeasing optical aspect, and with amounts more than 10 weight %, 45 50 55 60 65 70 75 80 85

troubles may arise during the thermo-processing step to form the sheet, and also the single particles can only with difficulty be discerned separately as distinctly as desired.

The thickness of the thermoplastic sheet may vary within a wide range which is generally from 2 to 2000 microns, preferably from 15 to 1000 microns, and especially from 25 to 750 microns.

Sheets having a thickness of from 2 to 20, preferably from 3 to 15, microns are advantageously manufactured by coating solutions or dispersions on a suitable carrier material, for example a thermoplastic sheet or paper, according to known methods, for example by means of rollers or screen rollers, casting and extrusion laminating equipment, with and without dosage, for example by knife or microjet roll coating devices, and subsequently eliminating the solvent or dispersing agent by drying.

In the case of thicknesses of from 20 to about 2000 microns, the known processes usual for the manufacture of thermoplastic material, such, for example, as extrusion, calendering or moulding, may be used to prepare the sheets containing the irradiation-converting particles; composite materials with other sheets or with paper may sometimes be advantageously manufactured immediately after the production of the sheets of the invention. Different luminous effects may be produced in the sheet formed by the coating and in the carrier sheet. A coating process is applied preferably in those cases where the irradiation-converting particles do not stand elevated temperatures and the shear stress usually occurring in thermoplastic processing.

Suitable particles which convert invisible electromagnetic irradiation to visible light (herein called irradiation-converting particles) may be those fluorescing upon excitation by ultraviolet rays. Examples are inorganic luminous substances such, for example, as sulphides, selenides, silicates and tungstates of the group II metals — the alkaline earth metals, zinc and cadmium — and calcium halophosphates, which contain traces of heavy metal, for example copper, silver, antimony, bismuth, tin, lead, titanium or manganese *per se* or as mixtures with themselves, furthermore the so-called Lenard phosphates. Activated zinc sulphide is especially suitable.

Organic luminous pigments may also be used unless they dissolve under the manufacturing conditions for the sheets, for example 2,5-bis-[5'-tert.-butyl-benzoxazolyl(2'')]-thiophene or di-benzo-oxazolyl-naphthalene, which are employed in aqueous dispersion in coating processes as referred to above. For other luminous

pigments suitable according to the present invention, see Ullmann Encyklopädie de Technischen Chemie, 3rd Edition (1960), vol. II, pp. 651—679; Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition (1967), vol. 12, pp. 619—625; and Römpp, Chemie-Lexikon, 7th Edition (1973), vol. 3, p. 1959.

Other suitable irradiation-converting particles include known materials which contain inorganic or organic irradiation-converting substances, for example plastics particles (grains, fibres or small rods), provided with optical brighteners, unless these materials dissolve under the manufacturing conditions for the sheets or coatings which are applied to the sheets.

The irradiation-converting particles need not necessarily have a distinct shape, and their size may vary within a wide range as defined above. A lower limit for the size is set only by the fact that in case of too small particles the luminous effect of the single particle is too faint to be perceived by the human eye without any auxiliary device.

In order to avoid processing troubles, the particle size (diameter) should preferably not exceed 4/5 of the thickness of the sheet containing the particles.

Also mixtures of different irradiation-converting particles may be used in a single sheet of the invention.

The insolubility of the irradiation-converting particles in the sheet mass may be a genuine property of the irradiation-converting substance, as in the case of zinc sulphide. However, it is also possible to produce this insolubility by dissolving or dispersing irradiation-converting substances, soluble or dispersible in the sheet mass, in other substances insoluble in the sheet mass, for example polymers, or by linking the first substances to the latter by absorption or chemical reaction in such a manner that they become insoluble or sparingly soluble even when the substances substantially insoluble in the sheet mass, for example polymer particles, are diffused during the processing of the sheet mass.

The irradiation-converting particles may be added to the plastic mixture ready to be processed according to known methods, for example in a fluid mixer. In special cases, the mixture may subsequently be ground gently in order to be homogenised; however, care has to be taken that the particles are not crushed. Similar care should be taken in subsequent processing steps where great shear stress occurs.

Suitable thermoplastics for the manufacture of the sheets are all normal thermoplastic polymers being substantially inert to the irradiation-converting particles, for example polystyrene; copolymers and graft polymers of styrene with acrylonitrile,

70

75

80

85

90

95

100

105

110

115

120

125

130

butadiene and acrylic esters; polyvinylidene halides such as polyvinylidene chloride or fluoride; polyamides; polyolefins such as polyethylene or propylene; polyacrylic and polyvinyl esters; thermoplastic polyurethanes; cellulose esters; polyvinyl chloride and copolymers or graft polymers of vinyl chloride.

Suitable monomers for a copolymerisation with vinyl chloride are for example: olefins such as ethylene, propylene or butylene; vinyl esters of unbranched or branched carboxylic acids having from 2 to 20, preferably 2 to 4 carbon atoms such as vinyl acetate, propionate, butyrate, -2-ethylhexoate, vinyl-isotridecanoic acid ester; vinyl halides such as vinyl fluoride, vinylidene fluoride or chloride, vinyl ether, vinyl pyridine; unsaturated acids such as maleic, fumaric, acrylic, methacrylic acid and the mono- or diesters thereof with mono- or dialcohols having from 1 to 10 carbon atoms; acrylonitrile, styrene, and N-substituted maleinimide. The copolymerisation may also be carried out using monomer mixtures.

For a graft polymerisation with vinyl chloride, there may be used elastomeric polymers obtained by polymerisation of one or more of the following monomers: dienes, such as butadiene, cyclopentadiene; olefins such as ethylene, propylene; styrene; unsaturated acids such as acrylic or methacrylic acid and the esters thereof with mono- or dialcohols having from 1 to 10 carbon atoms; acrylonitrile; vinyl compounds such as vinyl esters of unbranched or branched carboxylic acids having from 2 to 20, preferably from 2 to 4 carbon atoms; vinyl halides such as vinyl chloride, vinylidene chloride.

In case of copolymers or graft polymers, the amount of basic monomer, for example styrene or vinyl chloride, is advantageously at least 70 weight %, preferably at least 80 weight %.

These thermoplastics may be used *per se* or as mixtures with themselves. Furthermore, usual processing additives such as stabilizers, inhibitors, lubricants, plasticizers, solvents, dispersing agents etc. may be added as far as care is taken that the effect of the irradiation-converting particles is fully maintained and not suppressed by chemical alteration or a too high degree of general absorption of the active invisible electromagnetic irradiation.

If required or allowed by the application, the sheets of the invention may be dyed advantageously with pigments not converting the irradiation. It is recommended in this case to choose a color being very similar to that of the irradiation-converting pigments

in visible light, thus making the presence of these latter pigments substantially undiscernible in visible light without any auxiliary device.

Besides the irradiation-converting particles undissolved in the sheet mass, the sheets of the invention may contain one or more substances fluorescing upon irradiation with ultra-violet light in amounts of from 0.001 to 1%, preferably from 0.005 to 0.2%, relative to the total weight of the sheet; these substances, however, must be soluble in the plastic mass or dispersible in it in such a fine and uniform distribution that their fluorescence can be substantially and uniformly perceived with the naked eye over the total area of the sheet. Especially suitable for this purpose are optical brighteners, for example compounds having aromatic or heterocyclic ring systems substituted by benzoxazolyl radicals optionally substituted in the nucleus, or derivatives of cumarine or stilbene having optionally substituted benzotriazole or triazine radicals, which substances are substantially soluble in the sheet mass. The particles fluorescing in the invisible electromagnetic radiation which are present according to the invention in the plastic sheet appear as "starry sky" on a substrate shining in a different and preferably fainter shade.

Composite materials containing sheets having irradiation-converting particles are manufactured by moulding, welding or bonding; stamps optionally being applied simultaneously or subsequently.

The thermoplastic sheets of the invention may be used in all cases where inconspicuously marked sheets are required, for example as information carrier for the application of a printed and/or stamped image, an inscribable layer or a magnetic sound carrier. In the latter two cases, however, the inscribable or magnetic sound carrier layer is applied to one side of the sheet according to this invention, so that the irradiation-converting particles may be seen on the other side only of the composite material, unless the inscribable or magnetic sound carrier layer is itself provided with irradiation-converting particles. Preferably, the sheets of the invention are used as component of composite materials containing also other sheets and/or paper; these latter sheets or the paper serving as information carrier of the above kind. Photographs or other photomechanical reproductions may also be used together with the sheets of the invention.

The sheets of the invention are especially suitable for the manufacture of identity or credit cards or for similar applications.

Advantages of the sheets in accordance with the present invention are among others the simple and economic manufacture and

the inconspicuous marking which may be tested according to simple methods not destroying the particles. In the case where the marking has to meet more severe requirements, there may be used luminous spot counter devices which additionally are adjusted to distinct wave lengths of the light emitted by the irradiation-converting particles.

The following examples illustrate the invention, parts and percentages being by weight unless otherwise stated.

EXAMPLE 1.

A mixture of
 96 parts of polyvinyl chloride,
 3 parts of montanic acid ester wax,
 1 part of dibutyl-tin-dithioglycolate as stabilizer,
 6 parts of titanium dioxide, and
 0.5 part of luminous substance on the basis of zinc sulfide, mean particle size 18 microns,
 is homogenized for 2 minutes in a fluid mixer, plasticised on a roll mill at 150°C, and processed on a four roll calender at a temperature of from 160 to 180°C with a short-time heating to 220°C to form a sheet having a thickness of 0.3 mm. This sheet is pressed between heated plates at 170°C, and, after cooling, it shows a uniform purely white color on illumination with daylight or artificial light. Under a source of ultraviolet light however, the sheet appears as being dark and bespangled with spots shining brightly in a greenish color. A sheet made from the same mixture without addition of the luminous substance appears as a uniform dark surface in ultraviolet light.

EXAMPLE 2.

A mixture of
 56.5 parts of polyvinyl chloride,
 40 parts of a copolymer of acrylonitrile, butadiene and styrene (ABS),
 1.5 parts of dibutyl-tin-dithioglycolate as stabilizer,
 0.5 part of montanic acid ester wax,
 0.5 part of stearic acid,
 1 part of glycerol-mono-oleate,
 10 parts of titanium dioxide,
 2 parts of luminous substance on the basis of zinc sulfide, mean particle size 18 microns,
 is processed to a sheet having a thickness of 0.15 mm according to Example 1, the temperatures used in the calender being about 200°C. After cooling, the sheet shows a purely white color upon lighting with normal daylight or artificial light. Under a source of ultraviolet light however, the sheet appears as being dark and bespangled with spots shining brightly in a greenish color. A sheet made from the same mixture without addition of the luminous substance

appears as a uniform dark surface in ultraviolet light.

EXAMPLE 3.

A mixture of
 92.4 parts of polyvinyl chloride;
 6 parts of a copolymer of vinyl acetate and ethylene,
 1 part of dibutyl-tin-dithiocarboxylic acid ester,
 0.3 part of montanic acid ester wax,
 0.3 part of stearic acid,
 10 parts of titanium dioxide,
 0.05 part of di-benzoxazolyl-naphthalene,
 4 parts of luminous substance on the basis of zinc sulfide, mean particle size 18 microns,

is processed as described in Example 2 to form a sheet having a thickness of 0.5 mm. After cooling, the sheet shows a purely white color upon lighting with normal daylight. Under a source of ultra-violet light however, the sheet shines not too brightly in a bluish violet color and is bespangled with spots shining brightly in a yellow-green color, which spots clearly stand out against the substrate shining in a different color.

EXAMPLE 4.

A mixture of
 100 parts of a copolymer of acrylonitrile, butadiene and styrene (ABS),
 0.3 part of montanic acid ester wax,
 0.3 part of stearic acid,
 12 parts of titanium dioxide,
 0.005 part of 2,5-bis[5'-tert.-butylbenzoxazolyl(2')]-thiophene,
 8 parts of luminous substance on the basis of zinc sulfide, mean particle size 18 microns,

is heated in a heating/cooling mixer to 140°C, cooled and extruded on a single screw extruder, screw diameter 90 mm, having a slot die, at temperatures of the casing of from 170 to 180°C, to form a sheet which, after treatment at 85°C by means of smoothing rolls, has a thickness of 0.7 mm. The sheet has the same behaviour under daylight and ultraviolet illumination as described in Example 3.

EXAMPLE 5.

A sheet as described in Example 2, with without luminous substance, is coated with an aqueous dispersion containing 40% of a methylmethacrylate polymer with other vinyl compounds and 0.15% of dispersed di-benzoxazolyl-naphthalene having a mean particle size of 2 microns, at a rate of 5 g/m² of dry weight (about 4 microns of layer thickness), and dried in an air current at about 70°C. The coated sheet shows on both faces a practically identical white color under normal daylight or artificial light. Under a source of ultraviolet light, however,

the sheet appears to be uniformly dark on the uncoated face, and on the coated face it is bespangled with fine spots shining brightly in a bluish color.

WHAT WE CLAIM IS:—

1. A thermoplastic sheet containing undissolved particles which convert invisible electromagnetic irradiation to visible light, wherein these particles, optionally in the presence of soluble or insoluble, finely distributed fluorescing substances imperceptible *per se*, are present in such a small amount that on irradiation the luminous effect produced by an individual particle, separately from the luminous effect of other particles of the same kind, may be perceived with the naked eye on a substrate being either non-luminous or of a different luminosity, said particles having the form of grains, small rods, filaments or films, the grain size or thickness of the rods, filaments, or fibres, being in the range of from 0.3 to 600 microns, and the length of the rods, filaments, or fibres in a range of 0.03 to 20 mm.

2. A sheet as claimed in claim 1, wherein the amount of the irradiation-converting particles is in the range of from 0.03 to 10% by weight, relative to the total weight of the sheet.

3. A sheet as claimed in claim 2, wherein the amount of the irradiation-converting particles is in the range of from 0.3 to 2% by weight, relative to the total weight of the sheet.

4. A sheet as claimed in any one of claims 1 to 3, which has a thickness in the range of from 2 to 2000 microns.

5. A sheet as claimed in claim 4, wherein the thickness is in the range of from 15 to 1000 microns.

6. A sheet as claimed in claim 5, wherein the thickness is in the range of from 25 to 750 microns.

7. A sheet as claimed in claim 4, which is in the form of a coating having a thickness of 2 to 20 microns on a carrier material.

8. A sheet as claimed in claim 7, wherein the thickness is in the range of 3—15 microns.

9. A sheet as claimed in any one of claims 1 to 8, which contains at least two different irradiation-converting particles.

10. A sheet as claimed in any one of claims 1 to 9, wherein the irradiation-converting particles comprise particles of a salt of a metal of Group II of the Periodic Table, activated with a trace of heavy metal.

11. A sheet as claimed in claim 10, wherein the irradiation-converting particles comprise particles of zinc sulphide activated with traces of heavy metal.

12. A sheet as claimed in any one of claims 1 to 11, wherein the irradiation-converting particles comprise particles of 2,5-bis-[5'-tert.-butyl-benzoxazolyl(2')]-thiophene or di-benzo-oxazolyl-naphthalene.

13. A sheet as claimed in claims 1—12, wherein the grain size or thickness of the rods, filaments or fibres is in the range of from 0.5 to 100 microns.

14. A sheet as claimed in claims 1—13, wherein the grain size or thickness of the rods, filaments or fibres is in the range of from 1 to 30 microns.

15. A sheet as claimed in any one of claims 1—14, wherein the length of the rods, filaments or fibres is in the range of from 0.5 to 5 mm.

16. A sheet as claimed in any one of claims 1 to 15, which contains additionally one or more substances fluorescing upon irradiation with ultraviolet light in an amount of from 0.001 to 1%, relative to the total weight of the sheet, being present in the plastic mass in such a fine and uniform distribution that their fluorescence can be substantially and uniformly perceived with the naked eye over the total area of the sheet.

17. A sheet as claimed in claim 16, wherein the amount of fluorescing substance is 0.005 to 0.2% by weight.

18. A sheet as claimed in any one of claims 1 to 17, which contains additionally one or more optical brighteners substantially soluble in the sheet mass in an amount of from 0.001 to 1%, relative to the total weight of the sheet.

19. A sheet as claimed in any one of claims 1 to 18, which is dyed with a non-irradiation-converting pigment in a shade which in visible light substantially corresponds to that of the irradiation-converting particles.

20. A sheet as claimed in claim 1, substantially as described in any one of Examples 1 to 5 herein.

21. An information carrier comprising a sheet as claimed in any one of claims 1 to 20.

22. An information carrier as claimed in claim 21, which includes one or more other sheets and/or paper.

23. An information carrier as claimed in claim 21 or claim 22 which is an identity, cheque or credit card.

24. A composite material of different sheets which comprises a sheet as claimed in any one of claims 1 to 20.

25. A composite material of paper and one or more sheets comprising a sheet as claimed in any one of claims 1 to 20.

26. A composite material comprising a photograph or photomechanical reproduction and one or more sheets as claimed in any one of claims 1 to 20.

ABEL & IMRAY,
Chartered Patent Agents,
Northumberland House,
303—306 High Holborn,
London, WC1V 7LH.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.